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Effects of Alloying on Room-Temperature Tensile Properties of Tungsten-Fiber-Reinforced-Copper-Alloy Composites

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Relatively few metal-metal systems exist that would permit the creation of fiber-metal composites consisting of mutually insoluble constituents. It is anticipated that most high strength-to-weight ratio and high-temperature fiber composites ultimately to be produced will utilize high-strength fibers embedded in a highly alloyed matrix. An investigation was conducted to determine the effect of alloying on the tensile properties and microstructure of tungsten-fiber-reinforced composites. Composites were made of tungsten fibers infiltrated with copper binary alloys that contain elements of varying solubility in tungsten. Room-temperature tensile tests were made on the composites, and a metallographic study of the microstructure of the fiber-metal-matrix interfaces was conducted. It was shown that, as the depth of penetration of some alloying elements into the fiber increased, a decrease in both tensile strength and ductility of the composite results. A notch effect, due to the formation of a brittle alloy zone with the tungsten fiber, was observed and gave rise to greater reductions in tensile properties and ductility behavior than would be predicted by a law-of-mixture relation alone.

Author

IN recent years, investigators have considered combining fibrous materials with relatively weak binder materials. The interest in fiber-reinforced composites results from the fact that fibers or wires may be exceedingly strong and exhibit mechanical properties superior to those of the bulk materials from which they are derived. For example, tungsten wires drawn to less than 1 mil in diameter may have strengths of over 600,000 psi,[1] while steel wires ranging from 10 to 3 mils in diameter may have strengths of the order of 300,000 to over 600,000 psi.[2] Both metallic and ceramic whiskers are known to have very high strengths. For example, iron whiskers have been shown to have strengths of 1.9 million psi[3] and sapphire whiskers have been reported to have strengths of the order of 1.7 million psi.[4] If all or part of the strengths of such fibers could be retained, subsequent to the incorporation of the fibers in an engineering material, a superior material could result.

In previous work done at the Lewis Research Center, McDanels, Jech, and Weeton[5] demonstrated the feasibility of fabricating metal-fiber—metal-matrix composites that utilized the full strengths of the fiber and matrix materials. Tungsten fibers were combined with a copper matrix by a liquid-infiltration method such that the tungsten fibers were uniaxially oriented parallel to the tensile axis of the composite. A linear relation was established that related the tensile strength of the composite with the volume percent of the fibers. Mutually insoluble constituents were selected for the study so that the strength of the composite could be quantitatively related to the strength of the individual constituents.

The fact that there are only a few metals that are mutually insoluble with tungsten, *e.g.*, copper, silver, gold, and zinc, and that these either have low melting points, high vapor pressures, or poor oxidation resistance, makes it necessary to utilize other metals that are soluble in tungsten, where high-temperature applications are ultimately contemplated. It was anticipated that, for most practical fiber-reinforced composite materials, it would be necessary to use a fiber and metallic matrix that would have varying degrees of solubility for each other. A logical extension of the earlier work was thus felt to be a study that would determine the effects of elements that had mutual solubility with the tungsten.

Numerous investigators have found that tungsten fibers may be damaged by thermal treatments or contamination of the surface of the fiber by alloying elements.[6-10] On the other hand, surface treatments may improve the strength of such fibers.[11-13]

Relatively little work with composites containing tungsten fibers have been reported. The work of Parikh[14] has shown that kinked, short-length tungsten, steel, and molybdenum fibers could strengthen such matrices as silver, gold, and copper. Some of the combinations of fibers and matrices studied by

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Parikh had some solubility with each other, while others were insoluble. Pellegri[5] reported that the strength of several low-melting point metals and alloys could be increased by reinforcing them with steel wool. In a study by Jech, Weber, and Schwope,[16] a titanium alloy was reinforced with molybdenum fibers, and significant strength increases were obtained relative to the strength of the titanium alloy alone.

In the investigations reported above, some of the fibers and matrices studied were soluble in each other. These investigations, however, were not designed to determine the effects of alloying or solubility on the strength of the fiber or the composite.

From these considerations, it can be seen that work is needed to determine the strengths of composites as they are related to alloying reactions between the fiber and matrix materials. This investigation, therefore, was conducted to obtain an understanding of some effects of alloying additions made to fiber—metal-reinforced composite matrices. The intention of the bulk of the investigation was to determine some effects of differing alloying elements with differing solubility relation with tungsten on the tensile properties of tungsten-fiber-reinforced—copper-alloy composites.

In this investigation, copper was utilized as a carrier medium, that is, a medium to which alloying elements soluble in tungsten were added and transported to the surfaces of the tungsten fibers (in the liquid state) during the fabrication practice. The utilization of copper-base alloys as infiltrants permitted a study of the reaction of the element of interest on the surface of the fiber. Evaluation of the reactions of alloying elements added to the copper carrier were made possible by determining the tensile strengths of composites made from the fibers and alloy infiltrants and by making microstructural studies of the fibers within the composites. The strengths of the composites were then compared with strengths of mutually insoluble tungsten-fiber-reinforced—copper composites.

Composites were made of tungsten fibers infiltrated with copper binary alloys containing elements of varying solubility in tungsten: Al, Cr, Co, Nb, Ni, Ti, and Zr. The volume percent fibers contained in the composites ranged from 65 to 80 pct. Compositions of the matrix infiltrants were selected so that alloy melting points were 2100°F or less. Specimens were made by liquid-phase infiltration techniques at a temperature of 2200°F and for 1 hr in vacuum.

MATERIAL, APPARATUS, AND PROCEDURE

Fibers. Commercially pure tungsten wires (General Electric Type 218CS) of 0.005 in. diam were selected as the reinforcing fiber material. The wires were observed to have a room-temperature tensile strength of 330,000 psi after an annealing treatment at 2200°F for 1 hr in vacuum. This is the same strength value reported by McDanels, Jech, and Weeton[5] in their investigation after giving the wires an identical annealing treatment. The fibers were given this treatment to determine the thermal damage to the tensile properties of the tungsten fibers when infiltrated with copper at the same conditions. The infiltration temperature to be used in this investigation was the same as that of Ref. 5, so that a direct comparison can be made with the results of that investigation.

Infiltrants or Binder Materials. Copper-base binary alloys containing elements of varying solubility in tungsten were selected as matrix or binder materials so that a comparison could be made with the results of Ref. 5 in which pure copper was used as a binder. Any change in properties of a tungsten-fiber-reinforced composite using copper alloys as binders, relative to using copper as a binder, will thus be due to the alloying additions to the copper. The weight percent of an element alloyed to copper was limited by melting-point considerations. As was noted earlier, the temperature selected for infiltration was 2200°F. The amount of an element added to copper was thus selected so that the melting point of the alloy was below 2100°F. The compositions of the copper binary alloys selected as binders are given in Table I.

Specimen Fabrication. Bundles of 4-in.-long tungsten wires were cleaned to remove surface films and oxides by immersing in a hot, saturated solution of sodium peroxide and water, followed by rinsing in distilled water, immersing in a boiling solution of ammonia and water, and then rinsing again. The wires were then inserted into ceramic tubes so that the tube contained volume percents of wires ranging from 65 to 80 pct. The ceramic tube was placed in a closed-end quartz tube with a slug of the binder material to be infiltrated on the bottom. The entire assembly was then placed in a resistance-heated vacuum furnace and heated at 2200°F for 1 hr.

The composites thus obtained were tungsten fibers bound by matrices with varying degrees of solubility in tungsten. The specimens were 0.04 in. in diameter and contained continuous-length tungsten wires.

The specimens were then inserted into a 1/2-in.-deep hole drilled in a threaded rod. The specimens were brazed to the threaded rod using Aircosil number 45 (having a composition of 45 pct Ag, 15 pct Zn, 15 pct Cu, and 24 pct Cd and a melting point of 1125°F) as the brazing material. The specimen design is shown in Ref. 5. These specimens were then tested in tension at room temperature.

Test Procedure. Room-temperature tensile tests were made on the copper-alloy—tungsten-fiber composites with an Instron tensile machine (screw-driven) at a constant crosshead speed of 0.01 in. per min. A strip-chart recording of load against displacement was made for each test.

Reduction in area at the fracture edge of the composites was determined by measurements made with a comparator at a magnification of 100.

The procedure used for determining the relative amount of fiber or binder was to section the specimen after testing and then to measure the cross-sectional area of the specimen by planimetering a photograph of the cross section. This area was used as the basis for tensile strength calculations. A wire count was made of the cross section to determine the volume percent of the fiber present.

Metallographic Studies. Metallographic studies were made of the cross sections of tungsten-fiber-reinforced—copper-alloy composites. All the specimens were swab-etched with five parts NH_4OH plus one part H_2O_2 to reveal the copper-alloy structure, and Murakami's etchant (10 pct KOH, 10 pct $K_3Fe(CN_6)$, 100 cc H_2O) to reveal the structure of the tungsten wires. Photomicrographs were then taken at a magnification of 750.

Measurements of the depth of visible penetration, or depth of alloying of the binders with the tungsten fibers, were made on the etched cross sections of the composites at a magnification of 750 with a Filar eyepiece.

Electron photomicrographs were also taken of the cross section of some selected composites where views at higher magnifications were felt to be of interest. Parlodion replicas were made from specimens shadowed with chromium at an angle of 30 deg.

RESULTS

Tensile Tests. Room-temperature tensile-data plots for the copper-alloy—tungsten-fiber composites are shown in Figs. 1(*a*) to (*h*). The solid curve on each plot (a base line for comparison) represents the linear relation that was obtained in Ref. 5, which relates the tensile strength of pure copper—tungsten-fiber composites with the volume percent of

Table I. Room-Temperature Tensile Properties of Copper-Alloy–Tungsten-Fiber Composites

Binder Material	Maximum Solubility of Alloying Element in Tungsten	Wt Pct of Alloying Element	At. Pct of Alloying Element	Specimen	Vol Pct Fiber	Tensile Strength, Psi	Reduction in Area, Pct	Type of Fracture
Pure copper, Ref. 5	Insoluble in tungsten	0	0	—	65	225,700	—	Ductile
				—	70.2	238,000	—	Ductile
				—	75.4	249,800	—	Ductile
Copper-nickel	0.3	5	5.4	1	79	246,600	34	Ductile
				2	78.4	250,000	37	Ductile
				3	76	218,900	32	Ductile
		10	10.9	4	74.1	131,700	Nil	Brittle
				5	75.5	108,800	Nil	Brittle
				6	79.5	51,300	Nil	Brittle
Copper-cobalt	0.3	1	1.1	7	77.3	219,400	—	Semiductile
		5	5.4	8	76	213,200	1.5	Semiductile
				9	74.8	229,300	2.3	Ductile
				10	74.7	147,200	—	Brittle
				11	74.9	172,100	—	Brittle
Copper-aluminum	2.6	5	11.3	12	63.4	98,900	Nil	Brittle
				13	72.4	153,800	Nil	Semiductile
				14	76.1	154,500	Nil	Semiductile
		10	20.8	15	76.7	138,500	—	Brittle
Copper-titanium	8	10	12.8	16	78.2	223,700	—	Semiductile
				17	71.7	220,100	10	Semiductile
		25	30.7	18	76.3	186,700	—	Brittle
Copper-zirconium	3	10	7.2	19	72.8	216,000	Nil	Brittle
				20	78.5	255,300		Ductile
				21	75.6	226,900		Semiductile
				22	64.7	172,600		Brittle
				23	64.3	195,700		Semiductile
		33	25.5	24	75.9	106,700	Nil	Brittle
Copper-chromium	Complete solid solubility, miscibility gap	1	1.2	25	78.7	223,500	7.4	Semiductile
				26	77.5	228,600	25.8	Ductile
				27	77.2	225,900	7.5	Semiductile
		2	2.4	28	76.4	241,700	16.4	Ductile
Copper-niobium	Complete solid solubility	1	0.6	29	75.4	237,100	20.6	Ductile
				30	75.1	223,100	24.7	Ductile

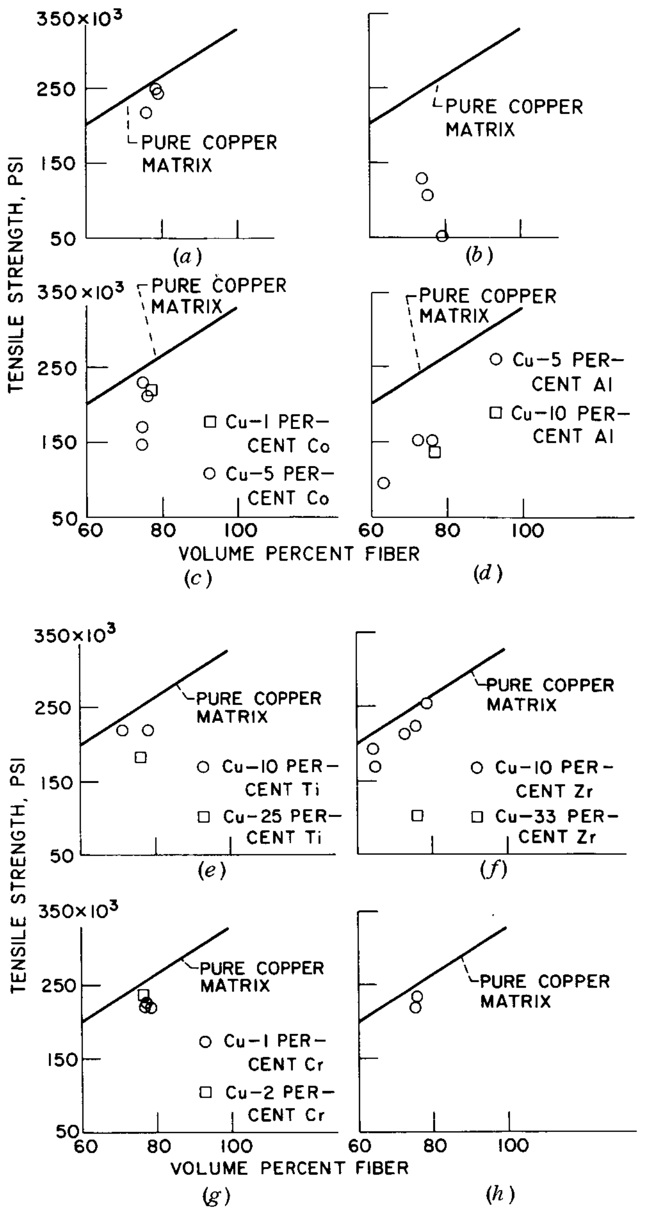


Fig. 1—Strength-composition diagrams comparing copper—tungsten-fiber composites to copper-alloy—tungsten-fiber composites. (*a*) Cu + 5 pct Ni matrix; (*b*) Cu + 10 pct Ni matrix; (*c*) Cu + 1 and 5 pct Co matrix; (*d*) Cu + 5 and 10 pct Al matrix; (*e*) Cu + 10 and 25 pct Ti matrix; (*f*) Cu + 10 and 33 pct Zr matrix; (*g*) Cu + 1 and 2 pct Cr matrix; (*h*) Cu + 1 pct Cb matrix.

the fibers in the composite or that might be calculated knowing the strength of the copper and tungsten fiber.

Table I compares the tensile strength, volume percent fiber content, reduction in area, and type of fracture of the copper-alloy—tungsten-fiber composite. It is evident that some copper alloys, namely, 5 pct Ni, 10 pct Ti, 10 pct Zr, 1 and 2 pct Cr, and 1 pct Nb, did not seriously effect the tensile properties of the composite. On the other hand, composites consisting of 10 pct Ni, 5 pct Co, and 10 pct Al, 25 pct Ti, and 33 pct Zr additions to copper, had a substantially lower tensile strength value than did the pure-copper bound specimens.

Fracture Ductility. The reduction in area of the composites as given in Table I was determined macroscropically by observing the fracture edges. It was difficult to obtain an exact value for the reduced area at the fracture edge because of the jagged fracture and wire "pull-out" at fracture. The reduction-in-area data obtained, however, indicate qualitatively the relative degree of ductility of the composites. Generally, it may be observed that those specimens that had the greatest degree of ductility at fracture exhibited the highest tensile-strength values. The photomicrographs, Figs. 2(*a*) to (*i*), show typical fracture edges of the composites. It should be noted that a measurable ductility can result from either the necking down of the composite at the fracture edge, as is evident in Fig. 2(*h*), or the necking down of individual fibers, as appears is the case in Fig. 2(*i*).

Load-Deformation Curves. Load-deformation curves were obtained for each specimen tested. Such deformation curves give a qualitative indication of the elongation as a function of load rather than a stress-strain curve, since they are made by measurements of the motion of the crosshead of the tensile machine. On the other hand, the shape of the curve indicates the degree of ductility that is observable at the fracture edge of the specimen; in fact, deformation curves were used to categorize fractures such as brittle, semiductile, and ductile. Fig. 3 shows such curves for the Cu 5-pct Co tungsten-fiber composites, and examples of the types of deformation are given in the figure.

Microstructural Studies. Microstructures of pure copper—tungsten-fiber specimen, Ref. 5, are shown in Fig. 4 to furnish a base line for comparison. Fig. 4 shows that recrystallization of the fibers has not taken place nor is any phase or alloying seen around the fibers, which would be expected since tungsten and copper are mutually insoluble.

Generally speaking, three types of reactions were observed to occur at the metal-matrix—tungsten-fiber interface.

1) A diffusion-penetration reaction accompanied by a recrystallization of the grains at the periphery of the tungsten fiber occurred. Such a reaction was evident for the specimens containing cobalt, aluminum, and 10 pct Ni additions to copper, as shown in Fig. 5. The recrystallization in the cobalt-containing matrices is different than in the nickel-containing matrices, not only in that subsurface recrystallization was produced, but that the recrystallization has occurred with the formation of smaller grains. The percentage of cobalt that lead to recrystallization of the tungsten fibers is much less than that for nickel. In fact, 5 pct Ni additions to copper did not produce a recrystallized tungsten zone, see Fig. 5.

2) A two-phase zone was formed. The two materials that produced such structures were the Cu-Ti and Cu-Zr binder materials shown in Fig. 6. Recrystallization of the tungsten was not evident in these specimens. The two-phase alloy zone formed by the reaction of the Cu-Ti binder with the

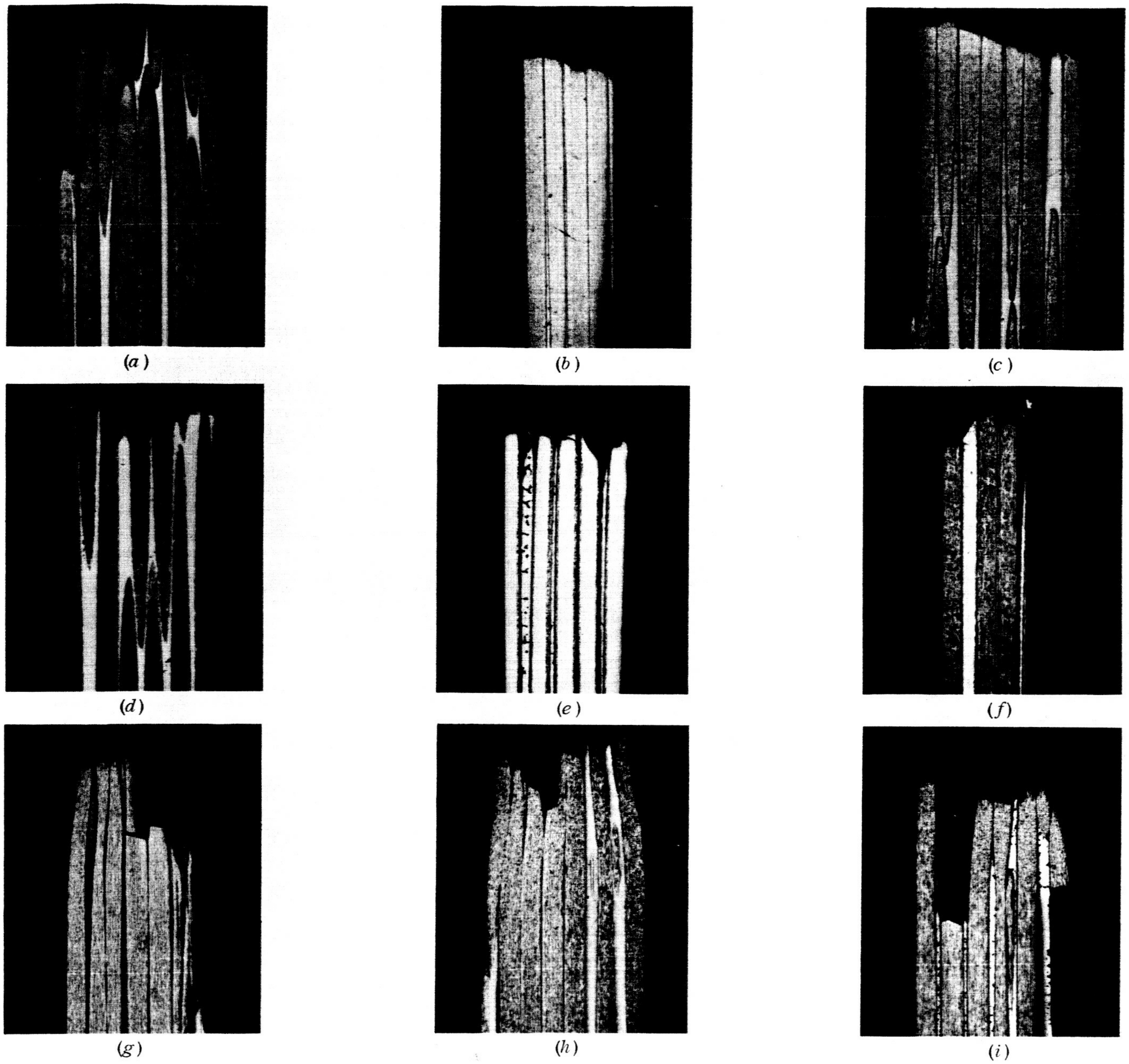


Fig. 2—Typical fracture edges of copper-alloy—tungsten-fiber composites. (*a*) Cu + 5 pct Ni; (*b*) Cu + 10 pct Ni; (*c*) Cu + 5 pct Co; (*d*) Cu + 5 pct Al; (*e*) Cu + 10 pct Ti; (*f*) Cu + 10 pct Zr; (*g*) Cu + 1 pct Cr; (*h*) Cu + 2 pct Cr; (*i*) Cu + 1 pct Cb.

fiber is resolved in the electron photomicrograph of Fig. 6. Higher titanium additives to copper, 25 pct, did not cause any recrystallization of the fibers to occur nor did higher zirconium additives, 33 pct. The higher titanium addition, however, resulted in a much larger alloyed fiber zone.

3) A solid-solution reaction without subsequent recrystallization took place. This type of interface reaction was largely that of a solid-solution reaction between the tungsten and the additive without any evidence of surface recrystallization. It was observed in the case of the Cu-Cr alloys, Fig. 7, and the Cu-Nb alloys.

Penetration Measurements. Table II lists the depth of penetration of alloys and the types of reactions that occurred at the metal-matrix—fiber interface and gives a quantitative indication of the extent of the attack or reaction. It is seen from Table II that the aluminum from the Cu-Al alloys penetrated to a greater depth than did any of the other copper alloys investigated. It is also evident that higher concentrations of a given element addition to copper gave increasing degrees of penetrations.

DISCUSSION

Tensile Strength Comparisons and Effect of Alloy Composition on Copper-Alloy—Tungsten-Fiber Composites Relative to Copper—Tungsten-Fiber Com-

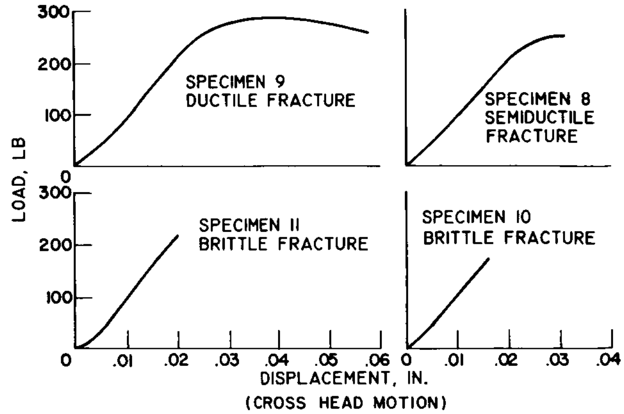
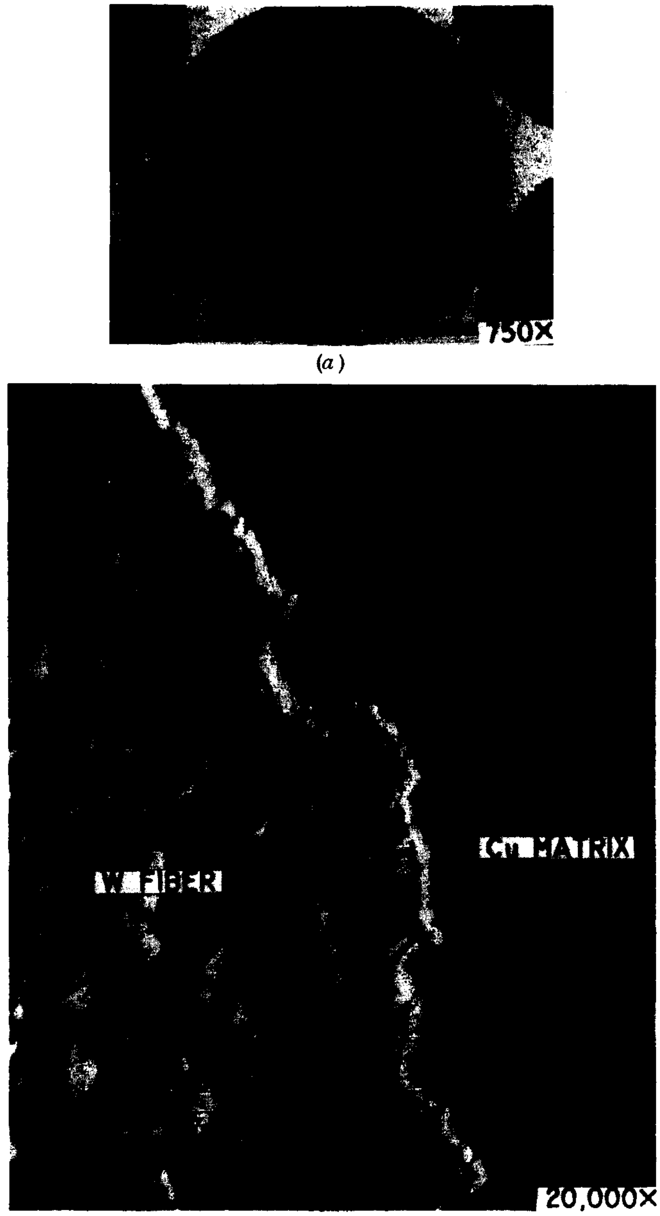


Fig. 3—Load as a function of displacement curves for tungsten-fiber-reinforced—Cu plus 5 pct Co composites.

posites. It was encouraging to find that several of the composites tested showed little reduction in tensile strength relative to the composites made from the insoluble materials, copper and tungsten, that were used as a base line for comparison. Thus, highly worked fibers may be combined with selected alloying elements without severely reducing their properties.

It should be noted from the values given in Table III that the Cu-33 pct Zr and Cu-25 pct Ti binders resulted in a large reduction in tensile strength. These composites were fabricated and tested to augment what appeared to be a possible alloying behavior noted in the early stages of the investigation. It was observed that low percentages of nickel additions to copper did not cause a recrystallization zone to form around the periphery of the tungsten fibers, whereas high percentages of nickel additions to copper did. It was also observed that additions to copper of 10 pct Zr or 10 pct Ti did not cause recrystallization zones to form. Since zirconium and titanium could be added to copper in large percentages without raising the melting point of the binder alloy, it was felt worthwhile to determine whether large percentages of these elements would also cause recrystallization. The metallographic results showed that these large alloy additions did not cause recrystallization although a larger alloyed zone was produced. The fact that these binders did significantly lower the tensile strength of the composites relative to the tensile strength of pure copper—tungsten-fiber-reinforced composites was almost certainly due to the brittle nature of the matrix material itself. In the case of the 33 pct Zr binder material, the matrix was almost entirely a brittle intermetallic, and in the case of the 25 pct Ti binder, large quantities of intermetallics were present. A discussion of the mechanism of damage to the tensile properties of the composite in these special cases will be made later. Thus, comparisons of damage to the fibers by alloying reactions with the fibers should be made only with the lower titanium and zirconium additions to copper, *e.g.*, 10 pct Zr, 10 pct Ti, which did not contain large quantities of intermetallic compounds.



(b)

Fig. 4—Copper—tungsten-fiber composites. Insoluble system. (*a*) Optical photomicrograph. (*b*) Electron photomicrograph of copper-matrix—tungsten-fiber composite.

The values in Table III, with the exception of these two binders, thus show clearly that the greatest damage by alloying reactions with the fiber was done by high percentages of nickel and by aluminum or cobalt additions to copper, and that much less damage was done by additions of titanium, chromium, zirconium, niobium, and low percentages of nickel.

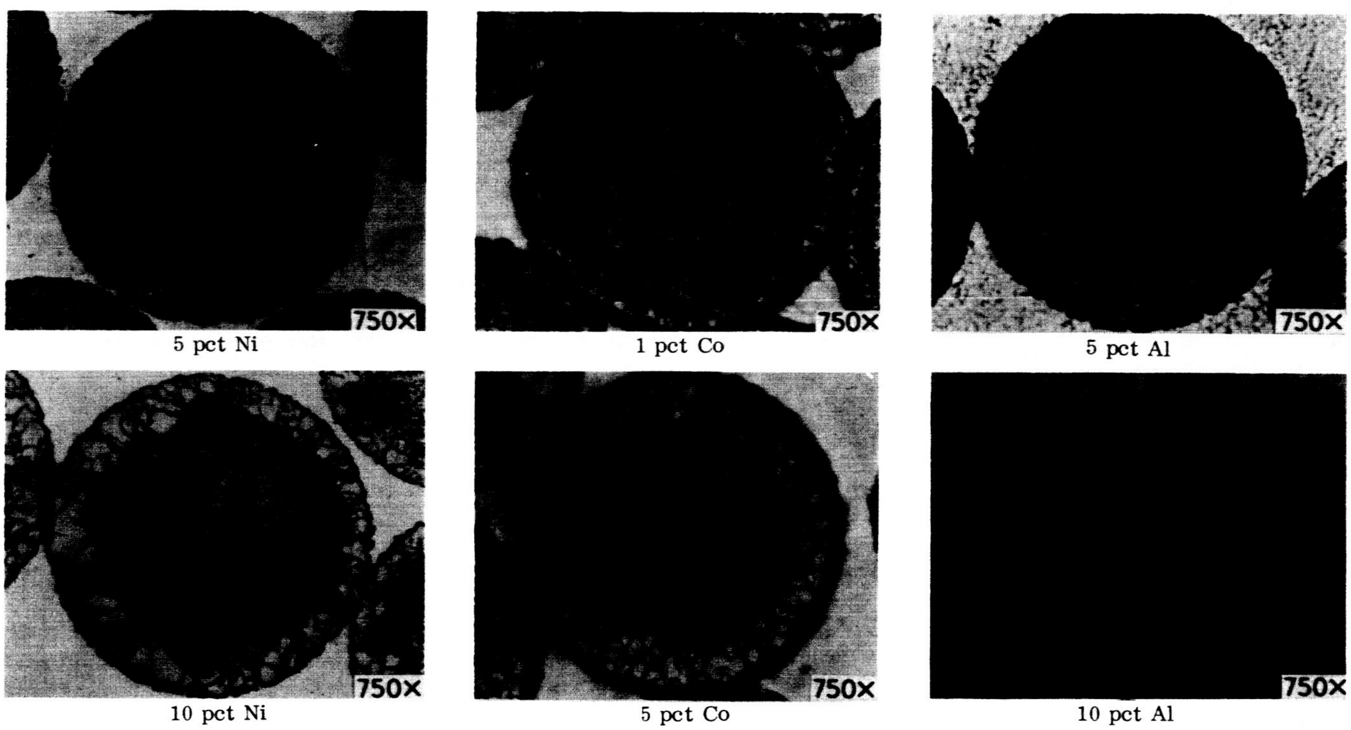
For a given alloy-matrix system with an increasing alloy content to the binder material, generally, there was an increasing degree of attack, or damage, to the composite structure, as is revealed in Table III.

Table IV shows the phase-equilibrium relations of the alloying elements, added to copper, with tungsten. It appears from the values of Tables III

Table II. Metal-Fiber Interface Reaction-Zone Measurements

Binder Material	Type of Reaction	Measurements of Reactions, Average Values: Recrystallization-Penetration Zone, In.	External Plate, In.	Two-Phase Zone, In.	Penetration Solid-solution Zone, In.
Cu- 5 pct Al	Diffusion penetration-recrystallization	0.0009	—	—	—
Cu-10 pct Al	Diffusion penetration-recrystallization	0.00104	0.000154	—	—
Cu- 1 pct Co	Diffusion penetration-recrystallization	0.000362	—	—	—
Cu- 5 pct Co	Diffusion penetration-recrystallization	0.000580	0.000138	—	—
Cu- 1 pct Cr	Penetration-solid solution	—	—	—	0.00011
Cu- 2 pct Cr	Penetration-solid solution	—	—	—	0.00011
Cu- 1 pct Nb	Penetration-solid solution	—	—	—	0.000052[a]
Cu- 5 pct Ni	Diffusion penetration	—	—	—	0.000052[a]
Cu-10 pct Ni	Diffusion penetration-recrystallization	0.000666	0.000238	—	—
Cu-10 pct Ti	Two-phase zone	—	—	0.000052[a]	—
Cu-25 pct Ti	Two-phase zone	—	—	0.000880	—
Cu-10 pct Zr	Two-phase zone	—	—	[b]	—
Cu-33 pct Zr	Two-phase zone	—	—	0.000052[a]	—

[a]Estimated.
[b]Not measurable.



(*a*) (*b*) (*c*)

Fig. 5—Copper-alloy—tungsten-fiber composites. Diffusion penetration-recrystallization reaction zones. (*a*) Cu + Ni matrix—W fiber composite. (*b*) Cu + Co matrix—W fiber composite. (*c*) Cu + Al matrix—W fiber composite.

and IV that the bcc materials did far less damage to the tungsten fibers than did the fcc materials. Of course, the fact that most of the bcc materials have melting points closer to that of tungsten, as well as the fact that they are isomorphous with tungsten, suggest that these materials should be more com-

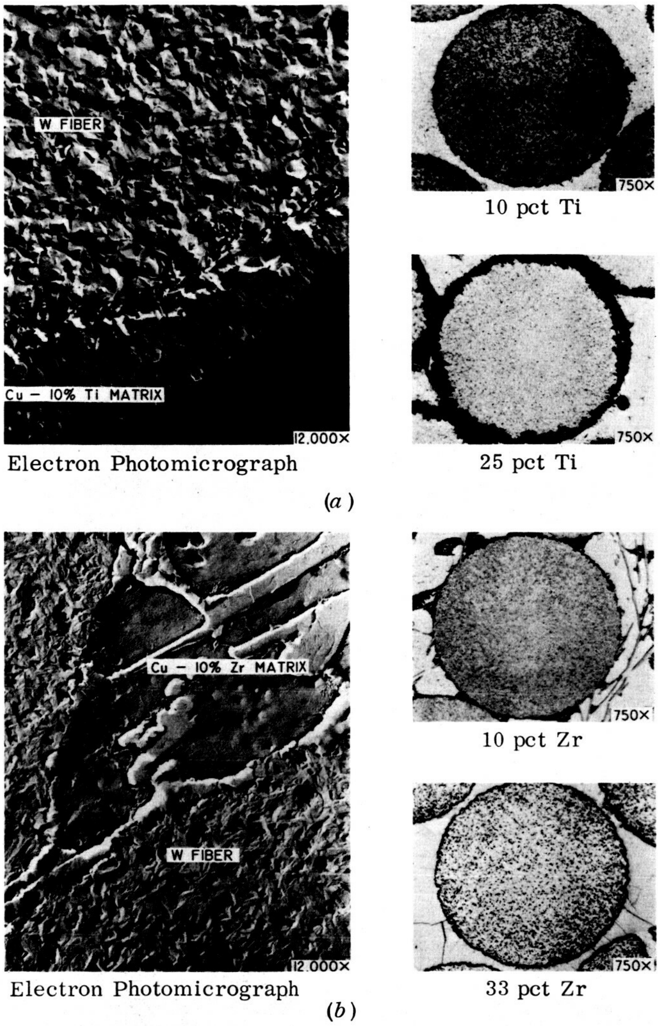


Fig. 6—Copper-alloy—tungsten-fiber compositions. Two-phase reaction zone. (a) Cu + 10 and 25 pct Ti + W fiber composite. (b) Cu + 10 and 33 pct Zr + W fiber composite.

Table III. Average Decrease and Percent Reduction in Tensile Strength of Tungsten-Fiber-Reinforced – Copper-Alloy Composites Relative to Tungsten-Fiber-Reinforced – Copper Composites

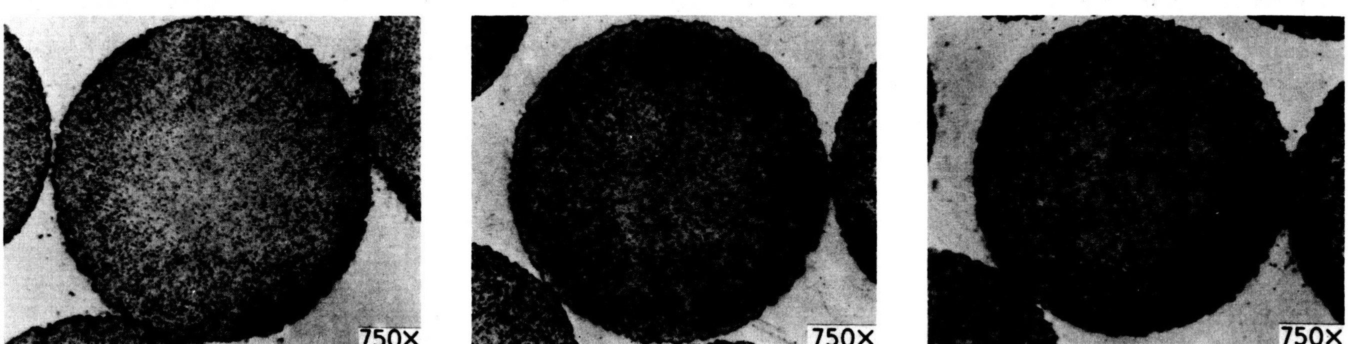
Binder Material	Average Decrease in Tensile Strength, Psi	Average Percent Reduction in Tensile Strength
Cu-10 pct Ni	160,000	62
Cu-33 pct Zr[a]	143,000	57
Cu-10 pct Al	117,000	46
Cu- 5 pct Al	100,000	43
Cu-25 pct Ti[a]	68,000	27
Cu- 5 pct Co	62,000	24
Cu-10 pct Ti	37,000	14
Cu- 1 pct Cr	30,000	12
Cu-10 pct Zr	25,000	10
Cu- 1 pct Nb	20,000	8
Cu- 5 pct Ni	17,500	7

[a]Although these alloys produced two-phase microstructures at the periphery of the fibers (within the fibers), the reduced tensile properties are believed to be the result of the embrittlement of the matrix by the large quantities of the alloying elements added to copper.

patible with tungsten and that they should have a lesser effect on the properties of tungsten. Furthermore, it is suggested that the depth of penetration and the degree of recrystallization would be less for materials that are relatively compatible with, or similar to, tungsten.

It can also be seen from Tables III and IV that the alloying elements that did the most damage to the properties of the fibers in the composites, namely, nickel, aluminum, and cobalt, had low solubilities in tungsten. Their atomic radii are also widely different (smaller) from that of tungsten, relative to most of the other materials investigated. This should be one indication that they would have a more rapid diffusion rate into tungsten than bcc materials with atomic radii close to that of tungsten. The combined damage that the fcc materials seem to have done to the tungsten fibers is believed to involve diffusion into the material and subsequent recrystallization of tungsten. It may also be noted that the solid solubility of tungsten in the elements studied is, in many cases, very large. This includes the cases of the materials containing cobalt and nickel plus other elements, which did not do much damage. The fact that the greatest damage to the composites was done by those materials where diffusion and recrystallization took place within the tungsten suggests that the solid solubility of tungsten in the binder materials is not as important a factor to consider as the solubility of the alloying elements in tungsten.

Correlation of Tensile Properties of the Copper-



(a) (b) (c)

Fig. 7—Copper-alloy—tungsten-fiber composites. Solid-solution reaction zone. (a) Cu + 1 pct Nb—W fiber composite. (b) Cu + 1 pct Cr—W fiber composite. (c) Cu + 2 pct Cr—W fiber composite.

Table IV. Phase-Equilibrium Relations

(Refs. 19 and 20)

Element	Melting Point °F	Melting Point °C	Crystal Structure	Maximum Solubility of Element in Tungsten, Wt Pct	Maximum Solubility of Tungsten in Element, Wt Pct	Eutectic Formation, °C	Probable Intermetallic
Al	1220	660	Fcc	2.6	1.5	—	WAl_7, WAl_{12}, W_2Al, WAl_3, WAl_4, WAl_5
Co	2723	1495	Hcp, below 788°F Fcc, above 788°F	0.3	45	1480	WCo_3, W_6Co_7
Cr	3430	1890	Hcp, below 82°F Bcc, above 82°F	Complete solid solubility (miscibility gap)		—	—
Nb	4380	2415	Bcc	Complete solid solubility		—	—
Ni	2651	1455	Fcc	0.3	45	1500	WNi_4
Ti	3300	1820	Hcp, below 1616°F Bcc, above 1616°F	8	50	1880	—
Zr	3200	1750	Hcp, below 862°F Bcc, above 862°F	3	8	1660	W_2Zr

Table V. Penetration-Recrystallization Zones Compared with Tensile Strength of Tungsten-Fiber-Reinforced — Cu plus 5 Pct Co Composites

Specimen	Penetration-Recrystallization Zone, In.	Tensile Strength, Psi	Volume Percent Fibers
9	0.000381	229,300	74.77
8	0.000425	213,200	75.96
11	0.000675	172,100	74.88
10	0.000840	147,200	74.73

Alloy—Tungsten-Fiber Composites with Microstructure. It was shown in the results that three types of phenomena were observed to occur at the metal-matrix—tungsten-fiber interface.

The type of reaction occurring at the copper-alloy—tungsten-fiber interface is given for every binder material investigated in Table II. The results clearly show that the most damaging type of reaction at the interface was the diffusion-penetration reaction accompanied by recrystallization. This type of reaction occurred with the Cu-10 pct Ni, Cu-1 pct and 5 pct Co, and Cu-5 pct and 10 pct Al binder materials. Solid-solution reactions without subsequent recrystallization did not seriously effect the tensile properties of the composites. The formation of a two-phase zone at the interface did not result in as great a reduction in tensile properties of the composites as did the diffusion-penetration accompanied by recrystallization reaction. It is interesting to note from Table III that the Cu-25 pct Ti binder, which formed a two-phase zone at the interface and which penetrated the fiber to a much greater depth than did either the Cu-10 pct Ni or Cu-5 pct Co binders, reduced the tensile strength of the composite 27 pct. However, the Cu-10 pct Ni binder and the Cu-5 pct Co binder reduced the tensile strength of the composites by 62 and 24 pct, respectively. The Cu-33 pct Zr composite had a two-phase reaction zone at the interface and resulted in reducing the tensile strength of the composite by 57 pct.

As was mentioned previously, another mechanism by which the strength of the composite may be damaged is associated with the ductility behavior of the matrix. It was indicated that some of the copper alloys are brittle because of the intermetallic content of the matrix. In the case of the Cu-33 pct Zr binder, cracks formed in the matrix and extended into the fibers. In addition, some of the fibers split in two. This splitting is believed to be the result of a stress-corrosion phenomenon.

Correlation of Depth of Penetration with Tensile Strength and Ductility Behavior. Depth-of-penetration measurements of the recrystallized-diffusion zones in the Cu-5 pct Co—tungsten-fiber composites are given in Table V. It can be seen that the depth of this zone varies even though the specimens were all given the same thermal treatment. It is known, however, from work of a preliminary nature done at the Lewis Research Center, that even a single strand of wire varies in its resistance to recrystallization at a given temperature. Thus, it is not surprising that varying degrees of recrystallization could take place by alloying. In measuring the depth of penetration of the recrystallization zones for the Cu-5 pct Co binders associated with the tungsten-fiber composites, it was observed that, as the depth of penetration of the recrystallized zone increased, there was a steady decrease in the tensile strength of the composite. The volume percent of fibers present in the composites is also approximately equal, as is noted in Table V. Thus, for a given fiber content, it was observed that, as the depth of penetration increased, a corresponding decrease in tensile strength was also observed. A decrease in the tensile strength of a composite due to alloying the fiber might be expected, since, by alloying the fibers, essentially, the true volume percentage of worked fiber in the composite has been

Table VI. Comparison of Ductility and Depth of Penetration with K

Alloy	Specimen	Type of Fracture	Change in Tensile Strength of Composite, $\Delta\sigma_c$, Psi	Cross-Sectional Area of Composite Occupied by Fiber, A_f, Pct	Twice the Depth of Penetration, P, In.	$K = \frac{\sigma_f - \sigma_p}{d_0^2}$, Lb Per In.^{4}
Cu- 5 pct Ni	1	Ductile	18,400	79	0.000106	223×10^{-8}
	2	Ductile	10,000	78.4	0.000106	122
	3	Ductile	36,000	76	0.000106	452
Cu-10 pct Ni	4	Brittle	115,800	74.1	0.00087	195×10^{-8}
	5	Brittle	143,000	75.5	0.00158	143
	6	Brittle	214,000	79.5	0.00155	206
Cu- 5 pct Co	8	Semiductile	42,000	76	0.00085	71×10^{-8}
	9	Ductile	21,000	74.8	0.00076	40
	10	Brittle	103,000	74.7	0.00168	99
	11	Brittle	78,000	74.9	0.00135	89
Cu-10 pct Ti	16	Semiductile	38,300	78.2	0.000104[a]	476×10^{-8}
	17	Semiductile	38,000	71.7	0.000104	515
Cu-10 pct Zr	19	Brittle	26,000	72.8	0.000104[a]	347×10^{-8}
	20	Ductile	5,000	78.5	↓	64
	21	Semiductile	23,000	75.6		296
	22	Brittle	43,400	64.8		645
	23	Semiductile	17,300	64.3		262
Cu- 1 pct Nb	29	Ductile	15,000	75.4	0.000104[a]	193×10^{-8}
	30	Ductile	28,000	75.1	0.000104	362

[a]Estimated value.

lowered. To obtain the same tensile strength as would have resulted if no alloying had occurred, the alloyed zone of the fiber must have the same tensile strength as the unalloyed portion. It is highly unlikely that the alloyed zone would have such a high tensile strength. The results of the investigation herein substantiate this. The degree of alloying with the fiber, thus, would determine the tensile properties of the composite: the greater the penetration, the greater the reduction in properties.

It was observed in a series of specimens with approximately the same volume percent fibers that the tensile strength and ductility varied with the depth of the recrystallized zone. To better understand the ductility behavior and tensile-strength reductions, as associated with recrystallization depths in the fibers, two approaches were taken. The first approach shows that the reduction in the properties of the cobalt specimens, as well as in some of the other systems, is not solely the result of a geometric effect (law-of-mixtures relation) associated with the area occupied by the recrystallized zone of the fiber. The composite should be considered a three-component system consisting of the Cu-Co binder, the unrecrystallized tungsten-wire core, and the recrystallized wire zone. If the strength of the recrystallized zone were known, the tensile strength of the three-component composite could be determined by using an equation similar to that presented in Ref. 5, and using the methods described in the appendix. The strength of the recrystallized zone was not known and therefore another approach was utilized. This approach is described in detail in the appendix and does not require a knowledge of the strength of the recrystallized zone. An equation was obtained that related the depth of the recrystallization-penetration zone with the loss in properties of a tungsten-fiber-reinforced—copper-alloy composite relative to a tungsten-fiber-reinforced—copper composite. This is shown as follows:

$$\Delta\sigma_c = KA_f(2Pd_0 - P^2)$$

where

$\Delta\sigma_c$ = difference in tensile strength between tungsten-fiber—copper composite and the tungsten-fiber—copper-alloy composite,

A_f = area percent fiber in cross section of composite,

$P/2$ = total depth of penetration or depth of recrystallized zone,

d_0 = initial diameter of fiber.

Thus, K should be constant for a given alloy system, if the penetration zone does not disproportionately damage the core of the fiber. To understand better the physical meaning of K, consider the relation derived in the appendix for K, namely Eq. [A4]: $K = \sigma_f - \sigma_p/d_0^2$. Obviously, on the basis of the assumptions needed to derive this equation, each term must be a constant. Values of K are given in Table VI. It is evident in the 5 pct Co binder system that there is a wide range of values of K, and, thus, the damage done to the composites

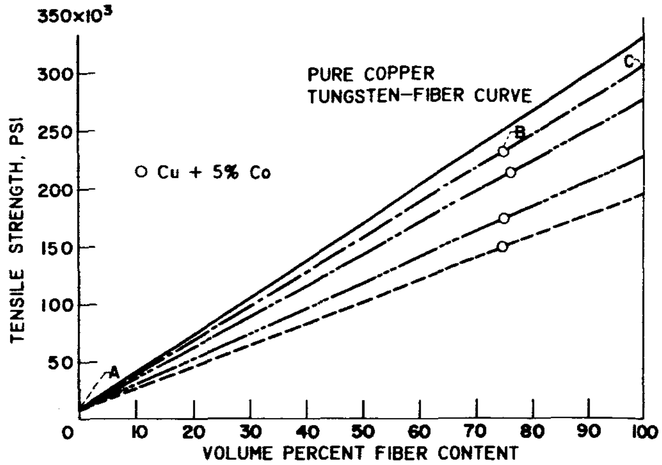


Fig. 8—Strength-composition curves for tungsten-fiber-reinforced—Cu plus 5 pct Co composite.

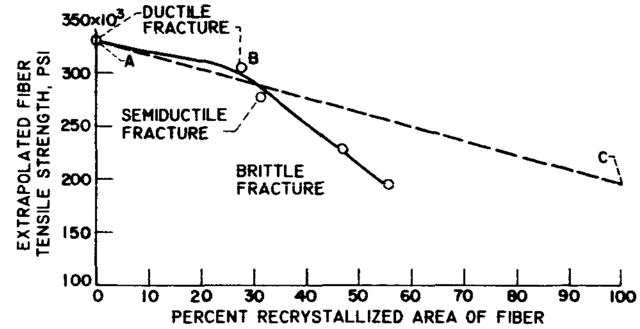


Fig. 9—Fiber tensile strength as a function of percent recrystallized area of fiber for Cu plus 5 pct Co composite.

is not solely related geometrically to the area occupied by the recrystallized zone. This is also true for binder materials such as Cu-Ni and Cu-Zr. It is felt that such a calculation would probably be significant for only those systems where three or more data points were obtained. In fact, it would be desirable to have many more data points for each system, but it was not the primary objective of this paper to prove this point. Consider, then, only the 5 pct Co, 5 pct Ni, 10 pct Ni, and 10 pct Zr systems for which several data points exist. In all these systems, a disproportionate amount of damage to the tensile-strength properties of the composites was observed, since K was generally larger at greater penetrations. It is also of interest to note that the fractures of the specimens showing the least reduction in strength were generally very ductile, whereas brittle fractures occurred for those specimens that have the greatest reductions in tensile strength.

The relation between the ductility and tensile strength of the individual tungsten fibers in a Cu-5 pct Co system and the depth of the recrystallization-penetration zone can also be determined by a graphical approach. The tensile-strength contribution of the fiber (the fiber in this case includes the recrystallized zone) to the tensile strength of the composite can be obtained by finding the value of the 100 pct tungsten-fiber content intercept on a plot of tensile strength against fiber content for the composites tested. This is shown in Fig. 8. Assume that the strength contribution of the copper alloys to the strength of the composite is the same as that obtained with pure copper as a binder. The tensile-strength contribution of the tungsten fiber to the tensile strength of the composite can be obtained by drawing a line from the pure copper—tungsten-fiber line intercept at zero percent fiber content, A, through the Cu-5 pct Co system data point, B, to its intercept at 100 pct fiber content, C. The 100 pct fiber-content intercept thus gives the value of the tensile-strength contribution of each individual tungsten fiber. This tensile-strength value is then plotted against the percent area of the fiber that is recrystallized, as is shown in Fig. 9. The tensile-strength value for an unrecrystallized tungsten fiber used in this study is known to be 330,000 psi. An approximation of the tensile strength of the recrystallized zone of the fibers, or of a fully recrystallized fiber, may be obtained by drawing a straight line between the tensile strength of the unrecrystallized tungsten fiber, A, and the tensile strength of the tungsten fibers in the two best Cu-5 pct Co specimens, B. This approach might be a warranted one if more data points existed for the curve of Fig. 9 and if more were known of the effects of grain growth on the notch sensitivity of the recrystallized zone. In addition, the fracture was ductile, as mentioned earlier. Point C in Fig. 9 is, therefore, an approximate value for the strength of the recrystallized fiber zone. This value lies close to a reported value of 156,000 psi for fully recrystallized unalloyed tungsten wire.[17] The type of fracture observed for each specimen tested is also indicated in Fig. 9.

If the system obeyed a law of mixtures, all the data points for the Cu-5 pct Co system should lie on such a straight line as ABC. It is observed, however, that this is not the case. As the depth of penetration increased, an increased deviation in tensile strength from line ABC may be observed. The ductility behavior is also seen to vary with depth of penetration. As the depth of penetration increases, ductility decreases. It is also of interest to note from Fig. 9 that a drastic deviation from the law-of-mixture curve does not occur until the fiber has been penetrated to a depth greater than approximately 0.0004 in. or until 30 pct of the fiber has been recrystallized.

In the case of composites with the Cu-5 pct Co binders, it was also observed that, as the depth of the recrystallization-penetration zone increased, ductility decreased, as was evidenced from the load against displacement curves shown in Fig. 3. A decrease in tensile strength with increasing depth of penetration was also observed. It is believed that the decrease in both tensile strength and ductility of the tungsten fibers and composites is a result of a notch effect. Tungsten is known to be notch-sensitive. The fact that greater penetration depths resulted in lowered ductility is compatible with concepts of notch sensitivity. For example, in the work of Form and Baldwin,[18] in which the effects of brittle skins on otherwise ductile metals were determined, it was found that the ductility behavior of a metal under the influence of various case depths followed virtually the same pattern as that of the metal (without a brittle skin) under the influence of various notch depths. As the penetration depth increased, the ductility decreased. This then may explain why the brittle skin dropped the ductility and tensile strength of the fiber more rapidly than would be expected from only the consideration of the area occupied by the skin.

Fully recrystallized tungsten wire is extremely brittle at room temperature. The recrystallized tungsten zone of the fiber in composites containing a Cu-5 pct Co binder thus was believed to act as a brittle skin. It is believed that the brittle recrystallized tungsten zone fractured or cracked early in the tensile test and that the crack acted as a circumferential notch in the wire.

Several specimens of the 10 pct Ni series had recrystallization-penetration zones comparable to those of the 5 pct Co series. The Cu-Ni specimens were damaged to a much greater degree than were the Cu-Co specimens (62 against 24 pct, see Table III). A larger recrystallized grain size and a greater concentration of alloying element in the tungsten present two possible explanations for this effect. As would be expected, a notch effect has also occurred in this system.

In the case of a group of specimens containing 5 pct Ni, it was observed that Specimen 2, which had a reduction in tensile strength of 10,000 psi, however, had, within experimental measurement capabilities, the same depth of penetration as Specimen 3, which had a larger amount of damage. It was observed, however, that three wires in Specimen 3 had a recrystallized zone, a fact which could account for the lower properties of this specimen.

In the case of the 10 pct Zr specimens, tabulated in Table VI, the reaction at the interface is one that does not result in a recrystallized fiber zone; however, a nonuniform amount of damage results since the values of K vary considerably. The fact that the binder material consists, in part, of the intermetallic $ZrCu_3$ is believed to contribute to the disproportionate amount of damage observed. It was observed that the Cu-33 pct Zr—tungsten-fiber composite had a tensile strength that was only 50 pct of that of a Cu-10 pct Zr—tungsten-fiber composite. The depth of penetration, however, was not appreciably greater in the higher zirconium-content composite. It should be noted that this brittle intermetallic phase could prohibit the full utilization of the strength of the fibers, since the matrix could fail before the fibers reach their ultimate strength. If the matrix fractures at an elongation that is less than the elongation at which the tungsten fibers fracture, then it is apparent that the matrix will fail first and result in the tungsten fibers carrying more than their proportionate share of the load.

It appears, from what has preceded and from values given in Table II, that all the specimens that have recrystallization-penetration zones greater than 0.0004 in. result in disproportionate damages to the properties of the fibers and that, in part, this is due to a notch sensitivity of the fiber.

CONCLUSIONS

This investigation was conducted to determine the effect of alloying on the properties and microstructure of tungsten fibers and tungsten-fiber-reinforced composites. Composites were made of tungsten fibers infiltrated with various copper binary alloys (copper was utilized as a "transport medium") containing elements of varying solubility in tungsten. The following conclusions were drawn from this investigation.

1) The mechanical properties of the copper-alloy—tungsten-fiber composites studied were reduced to some degree when alloying with the tungsten fibers occurred. Several of the composite systems tested, however, showed little reduction in tensile strength relative to composites made from the insoluble materials, copper and tungsten, that were used as a base line for comparison. Highly worked tungsten fibers may thus be combined with selected alloying elements without severely reducing their properties.

2) For a given copper-alloy—matrix system, it was observed that as the alloying-element addition to copper was increased there was generally an increasing degree of attack or damage to the properties of the fibers and composites.

3) Three types of reactions were observed to have occurred at the metal-matrix—tungsten-fiber interface:

a) a diffusion-penetration reaction accompanied by a recrystallization of the grains at the periphery of the tungsten fiber;
b) formation of a two-phase zone;
c) a solid-solution reaction without subsequent recrystallization.

Reactions of types *b* and *c* did not seriously affect the properties of the fiber or composites studied. The most damaging type of reaction observed was the diffusion-penetration reaction accompanied by recrystallization.

4) Fcc alloying elements (which were the only elements that produced a diffusion-penetration recrystallization reaction, and which have low solubilities in tungsten and may be expected to have higher diffusion rates in tungsten) were more detrimental to the mechanical properties of the composites than were bcc alloying elements. In contrast, bcc alloying elements, which have relatively high solubilities in tungsten and may be expected to exhibit low diffusion rates in tungsten, were less detrimental to the mechanical properties of the composites.

5) Another mechanism by which the composites strength may be damaged is associated with the ductility behavior of the matrix. It was indicated that some of the copper alloys are brittle because of the intermetallic content of the matrix. In the case of the Cu-33 pct Zr alloy binder, cracks were believed to form in the matrix and progress into the fibers. In addition, some of the fibers were split in two. This splitting is believed to be the result of a stress-corrosion phenomenon.

6) A correlation between the tensile strength and ductility of the composite was observed. In general, those materials that exhibited the best properties in tension had the greatest ductility. Tensile properties and ductility behavior were also correlated with depth-of-penetration measurements: the greater the depth of penetration of the alloying element into the tungsten fibers the lower the tensile strength and ductility of the composite. An equation relating loss in properties of a composite to depth of penetration of alloying elements into the fibers within the composite was derived by using law-of-mixture equations. Damage to the composite can be shown to be greater than that predicted by a simple law-of-mixture relation. This fact, along with observed correlations between ductility and tensile strength of the fibers in the composites, suggested that damage was due to a notch effect.

CONCLUDING REMARKS

Relatively few metal-metal systems exist that would permit the creation of fiber-metal composites consisting of mutually insoluble constituents. It is anticipated that most high strength-to-weight ratio and high-temperature fiber composites ultimately to be produced will utilize high-strength fibers embedded in a highly alloyed matrix. Many high-strength fibers gain a considerable portion of their strength from mechanical-deformation processes or thermal treatments and usually contain considerable strain energy. Thus it would not be surprising that, during incorporation of such fibers into a matrix, properties of such high-strength fibers may be considerably reduced by further thermal or mechanical treatments or perhaps by alloying reactions. The findings of this paper are, in some instances, very encouraging, in that it has been shown that a very highly stressed fiber will not necessarily be appreciably damaged by alloying reactions. Although all of the alloying additions (of soluble elements) made to the copper-base binder materials lowered the strengths of the composites, some alloying elements did not do more than a superficial damage to the fibers at temperatures at which other elements severely damaged the fibers. It should also be noted that the times, temperatures, and manners of infiltration were preselected arbitrarily, rather than optimized.

APPENDIX

DERIVATION OF A MATHEMATICAL EQUATION RELATING THE DIFFERENCE IN TENSILE STRENGTH BETWEEN A TUNGSTEN-FIBER—COPPER COMPOSITE AND A TUNGSTEN-FIBER—COPPER-ALLOY COMPOSITE WITH A LAW-OF-MIXTURES RELATION ASSUMED

The equation for the predicted tensile strength of a pure copper—tungsten-fiber composite, as given in Ref. 5, is:

$$\left.\begin{aligned} L &= \sigma_{c,\mathrm{Cu}}A_c = \sigma_m^* A_m + A_f\sigma_f \\ \sigma_{c,\mathrm{Cu}} &= \sigma_m^* A_m + A_f\sigma_f \end{aligned}\right\} \qquad [\mathrm{A1}]$$

where

L = load carried by composite,

$\sigma_{c,\mathrm{Cu}}$ = tensile strength of composite,

A_c = cross-sectional area of composite (=1),

σ_m^* = stress on copper matrix,

A_m = fraction of cross-sectional area of composite occupied by matrix,

σ_f = tensile strength of fiber,

A_f = fraction of cross-sectional area of composite occupied by fiber.

Assume that the contribution of the copper alloy to the tensile strength of the composite is approximately equal to that obtained when pure copper is used as a binder. An equation analogous to Eq. [A1] for a copper-alloy—tungsten-fiber composite in which the fibers are partly alloyed would be as follows:

$$\sigma_{c,\,\mathrm{Cu\ alloy}}A_c = \sigma_m^* A_m + \sigma_f(A_f - A_p) + A_p\sigma_p \qquad [\mathrm{A2}]$$

where

$\sigma_{c,\,\mathrm{Cu\ alloy}}$ = tensile strength of alloyed composite,

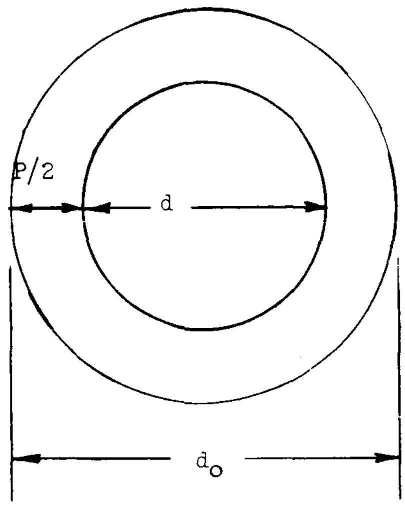
A_p = fraction of cross-sectional area of composite occupied by alloyed portion of fiber,

σ_p = tensile strength of alloyed zone of fiber.

The difference in tensile strength of a copper-alloy tungsten-fiber composite relative to a copper—tungsten-fiber composite with the same initial fiber content assumed is given by subtracting Eq. [A2] from Eq. [A1]. The following equation is obtained:

$$\sigma_{c,\mathrm{Cu}} - \sigma_{c,\,\mathrm{Cu\ alloy}} = A_p(\sigma_f - \sigma_p) \qquad [\mathrm{A3}]$$

Express Eq. [A3] in terms of the depth of the alloyed fiber zone, which is designated as $P/2$. The original diameter of the fiber is given as d_0, and the unalloyed zone as d (see sketch).



The symbol A_p may be expressed in terms of P and A_f (the original fiber content) as follows:

$$A_p = \left(\frac{d_0^2 - d^2}{d_0^2}\right)A_f$$

Since $d = d_0 - P$,

$$A_p = \left[\frac{d_0^2 - (d_0^2 + P^2 - 2d_0P)}{d_0^2}\right]A_f$$

$$A_p = \left(\frac{2d_0P - P^2}{d_0^2}\right)A_f$$

Substituting in Eq. [A3] yields

$$\sigma_{c,\mathrm{Cu}} - \sigma_{c,\,\mathrm{Cu\ alloy}} = (\sigma_f - \sigma_p)\left[\frac{A_f(2d_0P - P^2)}{d_0^2}\right]$$

Let

$$\Delta\sigma_c = \sigma_{c,\mathrm{Cu}} - \sigma_{c,\,\mathrm{Cu\ alloy}}$$

$$K = \frac{(\sigma_f - \sigma_p)}{d_0^2} \qquad [A4]$$

Then

$$\Delta\sigma_c = KA_f(2Pd_0 - P^2)$$

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